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# Tracing dissolved organic matter in a contrasted alkaline tropical wetland using fluorescence spectroscopy, Pantanal of Nhecolândia, Brazil

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## Abstract

The Nhecolândia is a sub-region of the Brazilian Pantanal wetland, where saline and freshwater lakes coexist in close proximity. Measurements of dissolved organic carbon (DOC) content and analysis of fluorescence excitation-emission matrices (EEM) were conducted in an effort to characterize spatial variability in concentration and source of dissolved organic matter (DOM). Increasing pH under the influence of evaporation resulted in an increasing DOC solubility ranging from 50 to over 300 mgC L<sup>-1</sup> in surface water. Spectrofluorescence characterisation indicates several families of dissolved organic matter, relatively stable in a given environment, but with contrasted signatures, which are related to the type of lake and its hydro-bio-geochemical functioning. Moreover, the fluorescence

signature from water and from the extracts of the surrounding soil samples shows strong similarities although disappearance of some labile proteinaceous compounds during humification. These results on the organic matter fluorescence EEM (stability, contrasted signatures and similarities between soil and related water samples) suggest that spectrofluorescence is a reliable technique for the tracing of water flows, but also for the marking of the origin of organic horizons in this environment.

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## 36 **1. Introduction**

In most hydrochemical functioning studies, inorganic chemical tracers are used to decipher the water pathways at the landscape scale. The recent technical development for chemical and isotopic tracing have ensured significant advances in surface hydrology and hydrogeology. However, although the number of chemical elements available for the tracing is large, the number of available tracers is limited, in practice, by their interaction with the solid phases and the biological activity, which can significantly affect the information carried by the chemical elements. Moreover, many of these elements behave similarly in a given environment and their use leads to redundant information.

Although the organic compounds are quickly degraded by biological activity, their wide range and diversity offer the possibility to consider their use as tracers or markers in some particular and favourable ecosystems. However, the difficulties in the characterisation of the organic compounds constitute a major challenge for their use in hydrochemical studies.

Spectroscopic techniques are widely used to acquire a first qualitative description of complex mixtures of organic compounds. Among these techniques, molecular fluorescence has gained a strong interest in the last decades (Powe et al., 2004). When UV-Visible spectrometry informs about the light absorption pattern of a sample, fluorescence introduces a second

descriptive pattern corresponding to the energy emitted in response to the excitation. This two-dimensional information enables the separate description (two different emission wavelengths) of compounds absorbing light similarly (identical excitation wavelengths). Emission scans recorded for a whole range of incrementing excitation wavelengths are used to create three-dimensional data sets called excitation-emission matrices (EEMs), representative of the total luminescence spectra. They are presented as contour maps of the fluorescence landscape with iso-intensity levels delineating various peaks. They can therefore be of great help to differentiate complex mixtures of fluorophores, based on their specific peaks. This technique has gained a lot of interest in the environmental field since Coble et al. (1990) first introduced its use for the study of dissolved organic matter (DOM) from sea waters. EEMs have since been recorded for numerous types of samples including humic acid in coral reefs (Matthews et al., 1996), saline soils (Cilenti et al., 2005), coastal and deep-sea sediments (Sierra et al., 2001), landfill leachates (Baker and Curry, 2004), farm wastes (Baker, 2002), natural waters (Marhaba et al., 2000; Parlanti et al., 2002) soil extracts (Cannavo et al., 2004) and tropical wetlands (Mladenov et al., 2005). As EEMs provide a detailed overview of the environmental samples, it is also used to trace the origin of individual DOM peaks (Katsuyama and Ohte, 2002; Stedmon et al., 2003; Alberts and Takacs, 2004; Baker, 2005; Sierra et al., 2005), to monitor organic contamination (Jiji et al., 1999) or the interaction between dissolved organic matter and metals (Dudal et al., 2006).

The objective of the present work is to assess if a comprehensive characterisation of dissolved organic matter could be used as tracer or marker of water flows and origins at the landscape scale. The Pantanal of Nhecolândia, Brazil, was selected for this study. This tropical wetland consists of thousands of lakes with very contrasted range of salinity and pH but coexisting in close proximity. The contrasted environmental conditions of the Nhecolândia, which has been recently the support for various studies in hydro-bio-geochemical sciences, are particularly

78 favourable for the application of spectrofluorescence to the discrimination and  
79 characterisation of dissolved organic matter.

80

## 81 **2. Study site**

82 The Pantanal wetland is a huge and still active alluvial plain situated between 16° and 20° S  
83 and 58° and 55° W, with a total area of about 200,000 km<sup>2</sup> of which 140,000 km<sup>2</sup> is located in  
84 Brazil. The vast tectonic depression of the Pantanal provides a gigantic natural flood control  
85 device for the storm waters resulting from torrential rainfall occurring during the wet period at  
86 the boundary between the Paraguay and Amazon basin. The plain, characterized by extremely  
87 low slopes (0.03 to 0.50 m/km) and altitudes between 100 and 200 m (Scott, 1991; Silva,  
88 1986) is partially reached by summer flood (November to March). During the dry season, the  
89 floodwaters recede, resulting in a complex mosaic of grasslands and forests dotted with  
90 countless lakes and marshes.

91 Quaternary sediments carried from surrounding highlands cover the plain along alluvial fans,  
92 built by the Paraguay river and tributaries (Del'Arco et al., 1982; Por, 1995). The  
93 Nhecolândia is one of the main sub-region (27 000 km<sup>2</sup>) of the Pantanal depression, located  
94 on the southern half of the Taquari alluvial fan. The sediments are mainly sandy (95%,  
95 Cunha, 1980) and the dominant soil orders are Spodosols and Entisols, both with less than  
96 15% of clay in superficial and sub-superficial horizons. These soils are locally associated with  
97 alkali soils (solonetz) with Na equivalent fractions higher than 15%.

98 The Nhecolândia includes about 12 000 round shaped lakes, among which Morisson et al.  
99 (2000) identified about 500 saline lakes, making up about 1 % of the total surface area of the  
100 region (Fig. 1). The co-existence of freshwater and saline lakes occurs mainly in the south  
101 western, lowland portion of Nhecolândia. The landscape is constituted by special features  
102 which will be referred throughout the article: 1- The freshwater lakes are temporary lakes of

the most variable forms and dimensions. They can reach approximately 2-m depths; 2- The temporary channels are formed by the coalescence of freshwater lakes during the flooding periods. They can be several kilometres long and 10 to 30 m wide; 3- The saline lakes are permanent rounded salt lakes that have generally 500 to 1000 m in diameter and are 2 to 3 m deep. Most commonly, they are isolated depressions inside sand hills, and they occupy the lowest topographical position of the landscape. 4- The sand hills are narrow (200-300 m wide), elongated, 2 to 3 m higher than the surrounding and covered by dense Savannah vegetation. These higher stripes of dry land are not submerged by superficial waters during flooding.

The ground water flows connecting the different lakes have been described by Barbiero et al. (2007). The saline lakes are encircled by a sandy clay horizon, with low permeability, high Na equivalent fraction and frequently indurated by amorphous silica. This horizon is rising up into the sand hill and behaves as a “threshold”, provoking a flow of water usually directed towards the saline lake. During the wet season, the water table rises and moves from the freshwater lakes and upland, into the sand and over the sandy clay horizon towards the depression of the saline lakes. On the contrary, during the dry season, the water table is lower and the sandy clay horizon acts as a barrier against the back flow of saline water towards the fresh sandy aquifer. The water flows towards the saline lakes and evaporates, and the ion contents increases in the saline lakes and the shore. The specific hydrological regime explains how saline and freshwater lakes having such different dissolved ion concentration, and subjected to the same amount of evaporation and rainfall, coexist in close proximity. The authors concluded that saline water results from present day evaporation and it is not necessary to resort to inheritance from arid period during the Pleistocene (Ab’Saber, 1988) to explain the presence of saline waters in some lakes of the Nhacolândia.

Drastic changes in the chemical profile of the water are observed at short distance, resulting from the above described local flows and evaporation. The less mineralised waters (freshwater lakes and temporary channels) can reach pH near to 5.5, and electrical conductivity about 0.02 mS.cm<sup>-1</sup>. They have a carbonate-chloride and sodic-potassic chemical profile. On the other hand the most mineralised waters (saline lakes and surrounding watertable) have pH values ranging from 9 to 10.5, an electrical conductivity from 4 to 20 mS.cm<sup>-1</sup> and a carbonate and sodic chemical profile. In addition, it was verified a significant decreasing of Ca<sup>2+</sup> and Mg<sup>2+</sup> activities in the most mineralised waters (Barbiero et al., 2002, 2007). Two independent processes have been identified as responsible for the geochemical control of Ca and Mg contents as the solution become more saline. One is the formation of Mg-calcite, and the other one is the precipitation of Mg-silicates, namely stevensite and saponite.

The tropical climate is of Aw type according to Koeppen's classification, with a mean annual temperature about 22°C and mean annual precipitation about 1000 mm mostly concentrated in summer (December to March). The mean annual evapotranspiration is around 1400 mm (Por, 1995; Alvarenga et al., 1984) resulting in an annual hydrological deficit of about 400 mm. At the local scale, the strong spatial variability of temperature and humidity according to land cover type (saline water, sand, savannah vegetation and grassland) induce a breeze system with diurnal and nocturnal alternation between the saline lake and the sand hills, increasing significantly the evapotranspiration (Quénol et al., 2005).

### **3. Material and methods**

#### *3.1. Fieldwork and Sampling*

The study was carried out at the Nhumirim experimental farm, which is known to be representative of the Nhecolândia's ecosystem. The wetlands selected for this study are

located between 18° 57' and 18° 59' S and 56° 37' and 56° 40' W. Samples have been collected in 6 waterbodies: 3 saline lakes, called Salina do Meio (SM), Salina do Oito (SO) and Salina da Ponta (SP), 1 lake with intermediate electrical conductivity called Salitrada (SL) and 2 freshwater lakes called Baia da Sede (BS) and Banhado (B). These lakes were selected so as to cover a large range of pH and conductivity. The distribution, shape and size of the lakes is presented on Fig. 1. Each lake exhibits special feature which will be used in the discussion. SM is a permanent saline lake with regular round shape and about 600 m in diameter. The electrical conductivity is regularly recorded since 1998 and ranged from 2.5 mS.cm<sup>-1</sup> during the rainy season to 15 mS.cm<sup>-1</sup> at the end of the dry season. SP is a permanent saline lake, which usually presents an electrical conductivity around 1/3 of that of SM. SO has a shape of “8” delimiting two units. The eastern part is permanent with EC values showing a large range from 2 mS.cm<sup>-1</sup> during the rainy season and up to exceptional values of 75 mS.cm<sup>-1</sup> during the driest period. The western part of the lake is occasionally drying during the dry season. A detailed geophysical study have revealed a seasonal subsurface entrance of freshwater into the western part of SO during the flooding period. The saline lakes are delimited by a white sandy beach induced by the high conductivity and the alkaline pH (above 9) of the water preventing from the development of vegetation. However, in the western part of SO, a grass vegetation is temporary developing down to the lake, when the freshwater is flowing in subsurface towards the saline lake. Microalgae are permanently (SM and SP) or periodically (SO) developing in the saline lakes (Souza Santos et al., 2004; Medina-Júnior and Rietzeler, 2005). Low redox conditions have been recorded ranging from -180 mV to +150 mV in the water, and from -370 mV to -200 mV in the sediment of these saline lakes (Barbiero et al., 2007).

Among the non permanent freshwater lakes, B is located along a temporary channel whereas BS is surrounded by “sand hills” with dense savannah. SL is supposed to be a former saline



lake, which has recently desalinised. Its electrical conductivity is monitored every year since 1998 and shows a decreasing trend from about 1.5 to 0.5 mS cm<sup>-1</sup>. Redox conditions are ranging from +150 mV to +380 mV in the water and about +200 mV in the sediments of the freshwater lakes. The depressions of B, BS and SL are covered by a grass vegetation and the lakes are temporarily occupied by floating and rooted emergent aquatic vegetation during flooding (Costa and Telmer, 2006).

Samples were taken in June 2006, i.e. at the beginning of the dry season, in each lake in order to estimate the internal variability of each system (saline: 23 samples; intermediate: 7 samples; freshwater lakes: 4 samples). Temperature (T), electrical conductivity (EC), redox (Eh) and pH were determined in the field before samples were filtered, collected in pre-washed polyethylene bottles and poisoned with HgCl.

Soil samples were taken in excavated pits around SM and SL in order to compare the soil organic matter with the DOM, to check for similar origins, and to estimate to which extent the organic matter is affected during the humification process. Both soil and water samples were kept frozen and stored in the dark until analyses within 30 days.

### *3.2. Laboratory work*

**Soil-water extracts:** For soil samples, a solution was extracted from a paste made of soil-water in a 1:5 weight ratio, after agitation (1 hour). The extracted solution was filtered through pre-combusted Whatman 2V glass fibre filters. The filtrate was subsequently passed through 0.45 µm nylon filters.

**DOM analysis:** Samples (5ml) were initially bubbled in acidic conditions in order to remove inorganic carbon. Dissolved Organic Carbon was quantified by combustion at 550°C using a Shimadzu TOC-meter (5050A fitted with laser CO<sub>2</sub> detector).

Fluorescence emission analysis: fluorescence data acquisition was performed using a Perkin-Elmer LS-55 Luminescence Spectrometer equipped with the FL Winlab Software. Excitation-Emission Matrices were collected every 10 nm over an excitation wavelength range of 200 - 600 nm, and a scan speed set at 1200 nm per min.

## **4. Results**

### *4.1. Dissolved organic matter contents*

The surface water DOC concentrations are high with a mean value reaching 192 mg.L<sup>-1</sup>, and a standard deviation of 118 mg.L<sup>-1</sup>, i.e. a coefficient of variation of about 61%. Large variations are observed depending upon the sampling location. Mean DOC values and standard deviation for each lake are plotted on Fig. 2. Three groups are easily discriminated. The first one consists of freshwater lakes (SL, B and BS) with low DOC contents. The pH values are ranging from 6.6 to 7.6 and conductivity from 0.15 to 0.5 mS.cm<sup>-1</sup> (Fig. 3). The second group consists of SO and SP, with higher electrical conductivity (1.5 to 2 mS.cm<sup>-1</sup>) and pH (8.6 to 9). The third one is SM, which has the highest pH values (9.6 to 9.8) and conductivity (3.5 to 4 mS.cm<sup>-1</sup>).

Examples of 3D-EEMs for the studied surface waters can be seen on Fig. 4 to 7. The results presented in Table 1 show that the type of EEM is contrasted between the different environments although the fluorescence peak positions were identical in one given waterbody, indicating low variability in the type of dissolved organic matter. In lake B, although low DOC have been recorded, high fluorescence intensity is observed (Fig. 5), suggesting the presence of humified organic matter, i.e. humic acids with high molecular weight and hardly degradable by biological activity. The peak positions ( $\lambda_{\text{ex}}$  /  $\lambda_{\text{em}}$ ) were estimated as 220 / 430 nm and 335 / 430 nm.

The fluorescence emissivity ( $F/[DOC]$ ) is much lower in SL (Fig. 4), where also low amounts of dissolved organic matter were detected (Table 1). It suggests that the organic matter consists likely of small stable fulvic acids.

The type of EEM observed in SM (Fig. 6) is clearly different from the previous ones, and in particular with two peaks observed at 230 / 340 nm and 290 / 350 nm, i.e. with emission domain typical of protein-like substances emphasising intense microbial activity. The same type of EEM was observed at SO and SP lakes, which appears therefore representative of the saline lakes.

Two different EEM signatures have been obtained in SO, opposing samples from the eastern part of the lake with EEMs similar to that of other saline lakes, and samples from the western part where the proteinaceous peaks are not detected, leading to an EEM similar to that observed with SL samples (Fig. 7).

#### *4.2. Particulate organic matter contents.*

The results of soil-water extracts from samples taken around SM and SL are presented on Fig. 8. A significant difference in the DOC extracted from SM and SL is obtained and the proportion of DOC found from the water of the corresponding lakes (SM and SL) are respected (Fig. 2 and 8). EEMs show similarities between DOC from water and from SM soil extracts (Fig. 6 and 9), with two peaks at about 270 / 460 nm and 380 / 450 nm, whereas the peaks previously identified at 230 / 340 nm and 290 / 350 nm have disappeared. Both DOC and fluorescence are high.

EEMs obtained after soil-water extraction from sediments around SL are very similar to EEMs obtained directly from collected water samples (Fig. 4 and 10) showing excitation-emission with the same wavelengths.

## 5. Discussion

The results obtained on the sampled lakes emphasized the interaction between inorganic and organic chemistry. A previous study carried out at the regional scale have shown a unique geochemical family of water evolving currently in an alkaline manner under the influence of evaporation (Barbiero et al., 2002). The geochemical composition changes from the weakly mineralised waters that flood the region during the rainy season, to the strongly mineralised and alkaline one in the saline lakes. The increase in the pH value favours the dissolution of organic matter and consequently high DOC contents are found there (average DOC values in saline lakes of  $262 \pm 118 \text{ mg.L}^{-1}$ ). Basic pH are known and used to dissolve natural organic matter and such high concentrations are therefore not surprising. Because the increases in the pH value is due to the evaporation process, these high DOC contents are also directly related to high electrical conductivities (Fig. 3). Moreover, the dissolved organic matter mainly consists in ionisable compounds due to the presence of a wide variety of oxygen containing functional groups. Usual pKa values for natural organic matter are determined by the two most abundant functional groups and are 4.7 (carboxyl group) and 10 (phenol group). Consequently, at the observed pH values the dissolved organic compounds are mostly anionic and are also partly contributing for the high electrical conductivity.

Along the concentration process of the water, three systems have been differentiated (fresh, intermediate and saline) and each shows a specific and contrasted type of dissolved organic matter, which is the result of physical-chemical and biological processes. In the saline-alkaline systems, that have not recently been fed by freshwaters (sampling was performed after a cumulative rainfall of 4 mm over three months and temperature averaging 30°C), the biological activity is strongly dominated by micro-algal vegetation as emphasized by a green colour clearly noticed during sampling in these stagnant waters. This is in line with the strong

presence of protein-like material observed from the fluorescence excitation-emission matrices of the saline lake waters (see Figure 6 and Table 1). Peaks at  $\lambda_{\text{ex}}$  230 –  $\lambda_{\text{em}}$  350 and  $\lambda_{\text{ex}}$  280 –  $\lambda_{\text{em}}$  350 nm have been related to the presence of the tryptophan and tyrosine (the two aromatic amino-acids) in proteins (Baker, 2002). Two aspects of the saline ecosystem contribute to the presence of labile proteinaceous material. On the one hand, the high algal activity permanently supplies such proteinaceous material, which is maintained by the fast turn-over in the biological cycle. On the other hand, the organic matter arising from micro-algae, consisting mainly of Cyanophytes, Chlorophytes, Chrysophytes and Euglenophytes (Souza Santos et al., 2004), has a low polymerisation rate with low molecular weight and therefore is easily degradable by the biological activity. The high velocity of organic matter degradation induces very reducing conditions, and the absence of oxygen could also explain the persistence of labile proteinaceous material. The strong microbial activity seems to be a peculiarity of the saline lakes.

The input of freshwater in this system has interesting implications regarding its biogeochemical functioning. These implications are revealed in SO, where such an entrance has been detected at the west end of the lake (Fig. 1). The freshwater has a pH value around 6.8 and an electrical conductivity of about 60 to 80  $\mu\text{S}\cdot\text{cm}^{-1}$ . Samples from the lake taken in this area allow us to observe the evolution: decrease in pH (7 instead of 8.8 in average for the rest of the lake), decrease in DOC content (120  $\text{mg L}^{-1}$  instead of about 250  $\text{mg L}^{-1}$  in average for the rest of the lake) and total disappearance of the proteinaceous fluorescence peaks (Fig. 7). Only the longer wavelengths peaks ( $\lambda_{\text{ex}}$  220 –  $\lambda_{\text{em}}$  425 and  $\lambda_{\text{ex}}$  330 –  $\lambda_{\text{em}}$  440 nm) are still present, showing a more stable type of organic matter (Baker & Curry, 2004). This behaviour is comparable to the one observed in SL (Fig. 4 and Table 1), which is intermediate to the freshwater lake type. The similarity in the EEMs between SL and the west end of SO is in

299 agreement with the 8-year salinity monitoring carried out in SL that suggests a former saline  
300 lake currently following a dynamic of de-salinisation.

301 The freshwater lake B is characterised by neutral pH freshwater, with high fluorescence in the  
302 longer wavelengths (Fig. 5) corresponding to highly stable “humic-type” aromatic material  
303 (Parlanti et al., 2002). In this system, no algal development is observed, and vegetation is  
304 found all around, which contributes to the lignin-type compounds found in the fluorescence  
305 excitation-emission matrices (Sierra et al., 2005). The higher redox values and the slow  
306 humification of the polymerised organic matter favour a fluorescence with peaks on a wider  
307 wavelengths range.

308 The stability of the DOM signature in each system is emphasized by the data from the 34  
309 samples presented in table I. The stability suggests that the use of the spectrofluorescence  
310 technique is relevant to trace the origin of the organic matter in this apparently complex  
311 ecosystem.

#### 312 313 *Particulate versus dissolved organic matter*

314 Several modes of organic matter accumulation are possible in the Pantanal environment,  
315 namely simple sedimentation in lakes with various pH-EC conditions, burying of former  
316 topsoil horizon with organic matter of various origin, migration of dissolved organic matter  
317 under alkaline conditions and accumulation due to a pH-barrier or because of intense  
318 evaporation. Although the spatial variations in the pH values seems to have a major influence  
319 in the control of DOC content, the nature of the organic matter could be different according to  
320 its origin.

321 From a quantitative point of view, the dissolved organic matter in the soil water extracts  
322 confirms the results described in the water samples, i.e., higher values are observed in extracts  
323 from alkaline systems than from freshwater systems. It suggests that part of the organic matter

from the sediments (organic acids with low molecular weight) can be easily remobilised by the water during the flood period.

Moreover, and from a qualitative point of view, strong similarities are detected in the fluorescence signature of the organic matter between samples from soil extracts and water. In both water and soil-water extracts from SL, the organic matter consists of small stable acids, probably fulvic acids or association of phenolic acids, in low quantity and with low fluorescence emissivity. In SM, the similarity between water and soil water extracts is still observed, except for the most labile proteinaceous material. It seems that when the lake is drying, the oxygenation of the sediment affects only a part of the fluorescence signature consisting of the labile compounds but preserve the non proteinaceous material. The organic matter collected around the lakes maintained the signature of its origin. As a consequence, a certain persistence of the organic matter signature is occurring and it emphasises the relevance of the spectrofluorescence technique to trace the origin of the organic matter.

## **6. Conclusion**

The shallow groundwaters of the Nhicolândia are relatively depleted in calcium with respect to alkalinity and evolve into high alkalinity and high pH as solutions become more saline under the influence of evaporation. The increasing pH results in an increasing solubility of the organic matter, and consequently to a strongly structured distribution of the organic matter in the landscape. The freshwater lakes surrounding by herbaceous vegetation have low dissolved organic matter contents, whereas the alkaline lakes surrounded by a sandy beach sterilised by high pH and conductivity have much higher dissolved organic matter contents. The spectrofluorimetric characterisation shows several families of organic matter, which are relatively stable in space. The freshwater environments exhibit humic acids with strong

fluorescence, whereas the saline alkaline environments have very different functional groups and proteinaceous material.

The organic matter contents and its characteristics are closely related to the biological functioning of the waterbodies. It is also noticeable that the organic matter sampled around and in the lakes showed similar fluorescence characteristics, highlighting a certain stability of the criteria for organic matter characterisation. Only some labile functional groups, such as proteins, disappear during the maturation in the soil.

Because of the stability of the parameters used for the discrimination, spectrofluorescence is a reliable technique for the tracing of water flows, but also for the marking of the origin of organic horizons.

The study reveals the influence of the herbaceous vegetation around and in freshwater lakes and algal vegetation in saline lakes, but the influence of the forest in the sand hill has not been detected. Further study should focus on this point in order to better understand the migration of carbon in this environment.

Previous study in this area have shown a strong spatial heterogeneity in the inorganic chemistry attributed to physico-chemical processes. The results of the present study also show the heterogeneity in the distribution of the organic matter, but attributed to the interactions between physico-chemical conditions and the biogeochemical functioning of the landscape units.

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Fig. 1 : Aerial view of the study site (dry season) : sampled waterbodies are SM (Salina do  
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da Sede). The arrow denotes the seasonal entrance of freshwater into SO.

Fig. 2. Dissolved Organic Carbon from the studied lakes: SM = Salina do Meio, SO = Salina  
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Fig. 3 : Relationship between Dissolved Organic Carbon and Electrical Conductivity of the  
studied lakes.

Fig. 4 : Excitation-Emission Matrice of the lake Salitrada (SL) - Note the low reactivity of  
the organic matter.

Fig. 5 : Excitation-Emission Matrice of the lake Banhado (B) - Although the DOC content is  
low, note the high reactivity of the organic matter.

Fig. 6 : Excitation-Emission Matrice of the lake Salina do Meio (SM) – Note the  
fluorescence at about  $\lambda_{ex}=230\text{nm}$  and  $\lambda_{ex}=290\text{nm}$  corresponding to proteinaceous material.

516

517 Fig. 7 : Excitation-Emission Matrices of the lake Salina do Oito (SO) showing the differences  
518 between the eastern saline part of the lake (b) and the western part (a) where an entrance of  
519 freshwater have been detected.

520

521 Fig. 8 : Organic Carbon contents from soil-water extracts in the Salina do Meio (SM) and  
522 Salitrada (SL) lakes.

523

524 Fig. 9 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salina do  
525 Meio (SM) – Note the similarity with Fig. 6 and disappearance of peaks of proteinaceous  
526 material.

527

528 Fig. 10 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salitrada  
529 (SL) – Note the similarity with Fig. 4.

530

531 Table 1. Dissolved organic matter's characteristics

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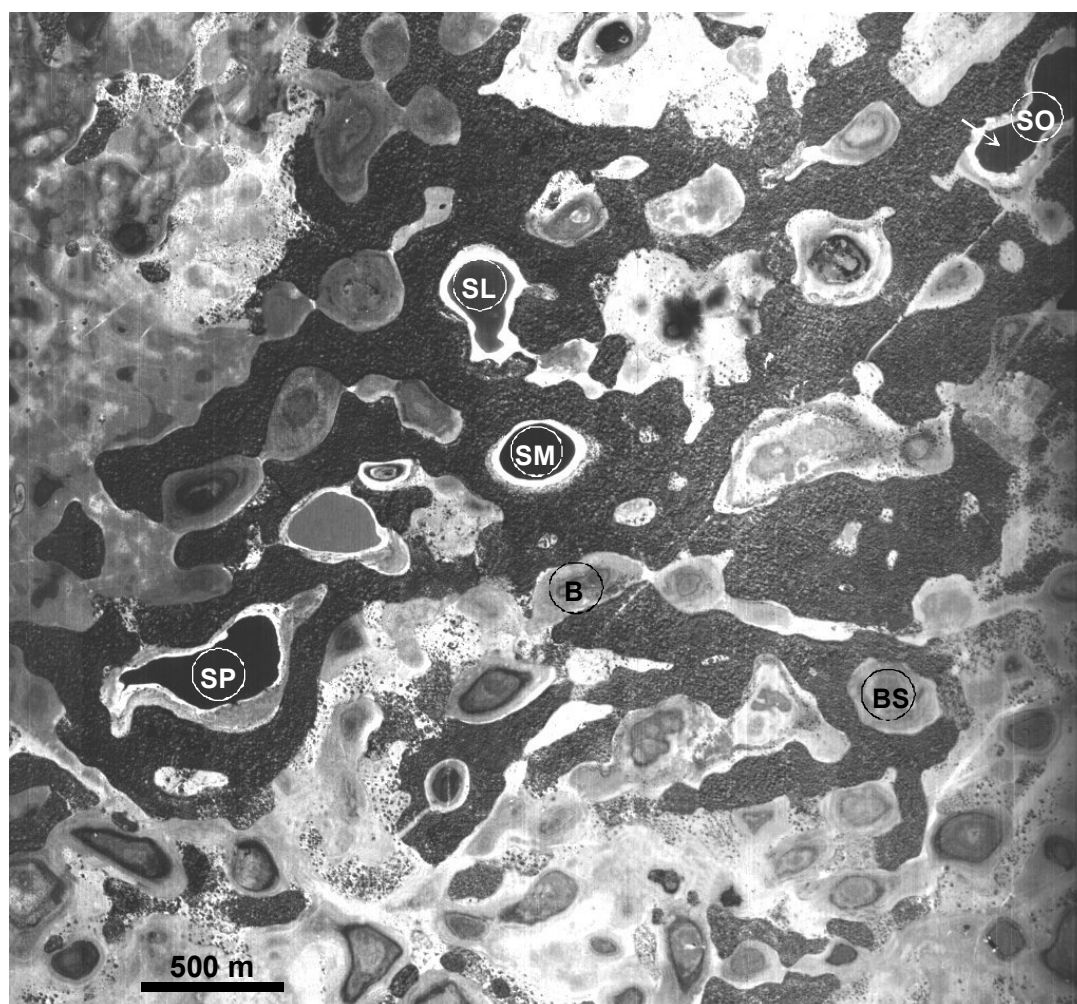


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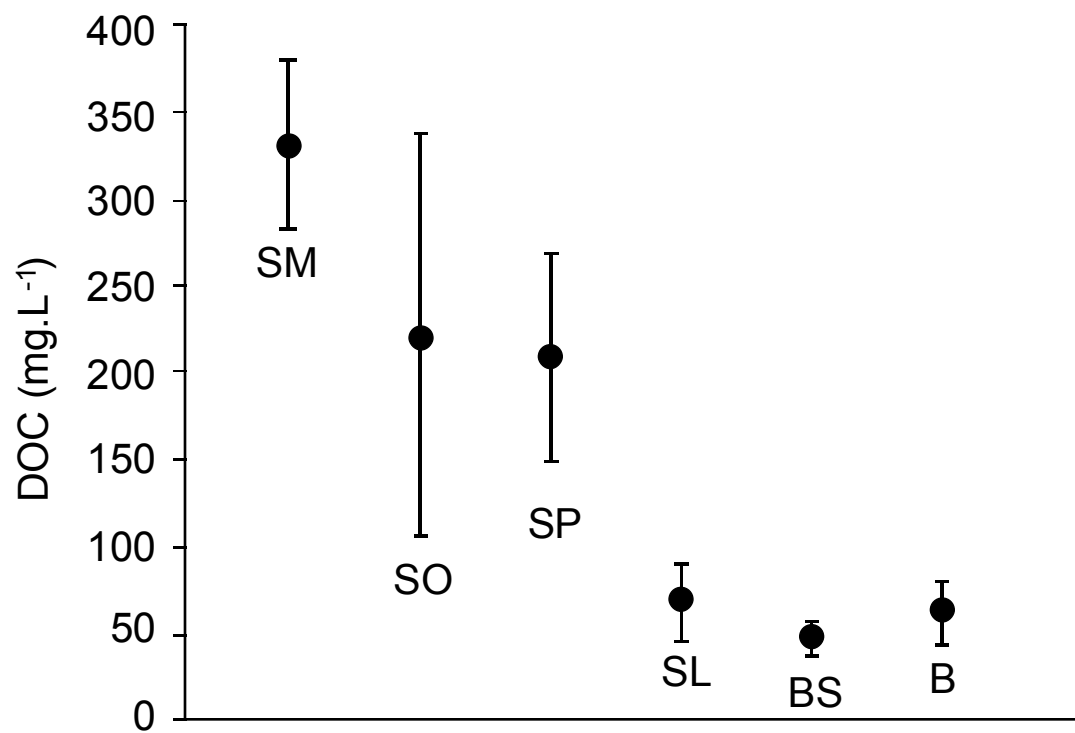


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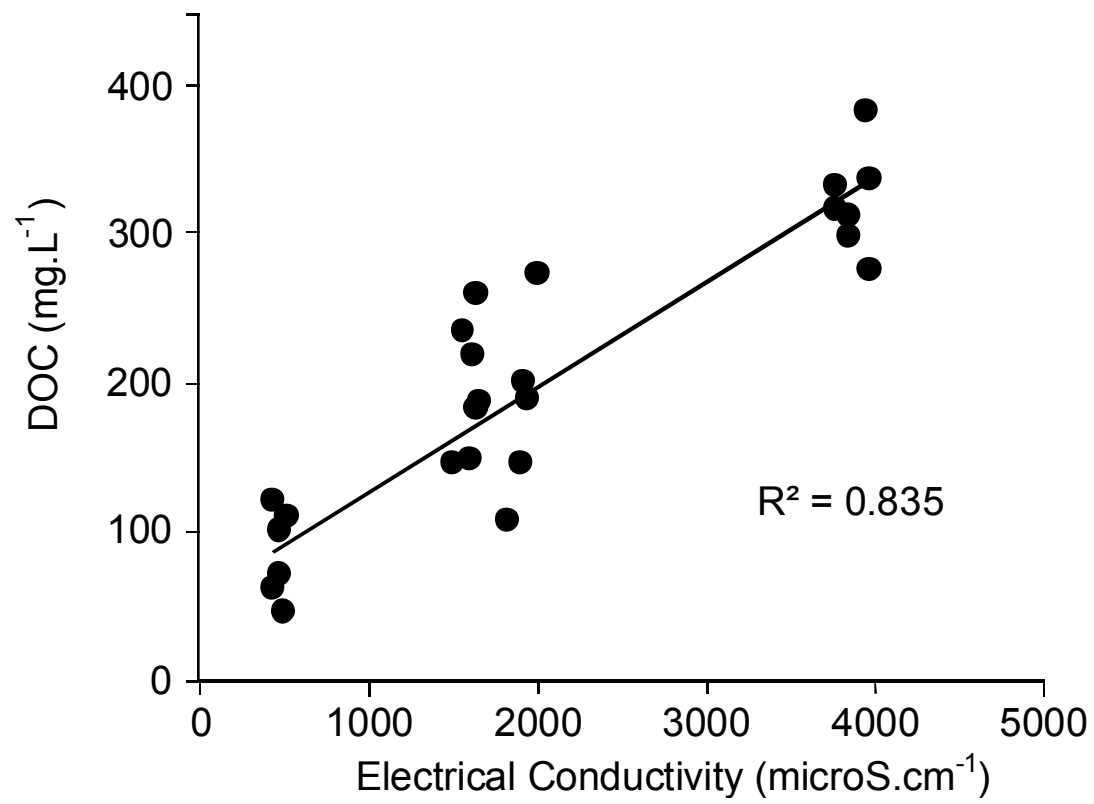


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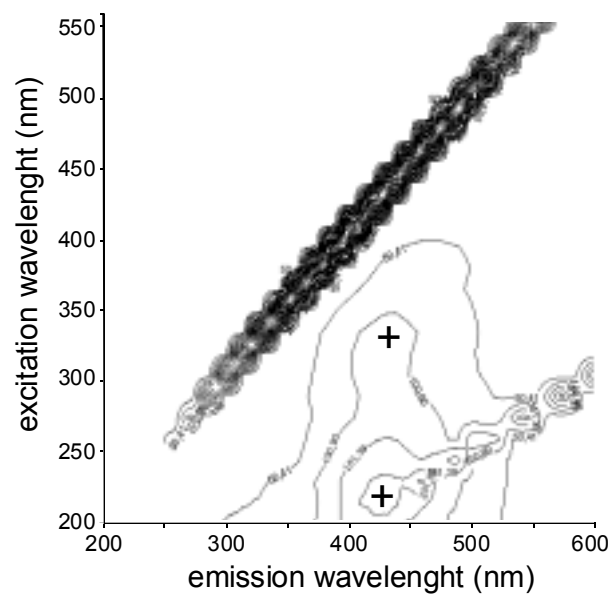


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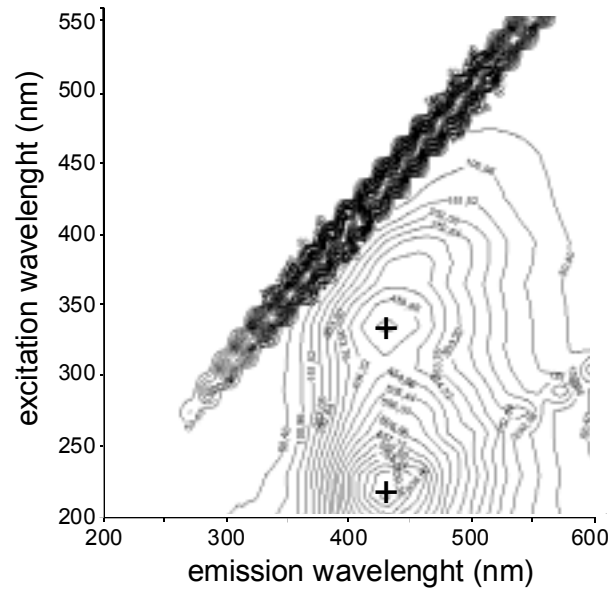


Fig. 5 : Excitation-Emission Matrice of the lake Banhado (B) - Although the DOC content is low, note the high reactivity of the organic matter.

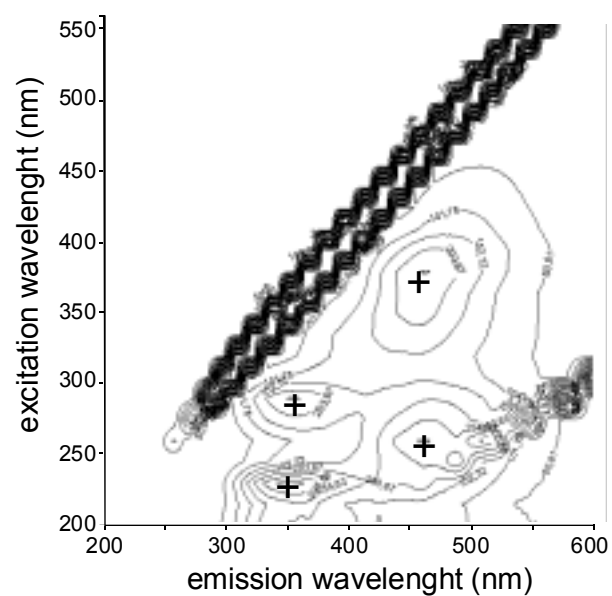


Fig. 6 : Excitation-Emission Matrice of the lake Salina do Meio (SM) – Note the fluorescence at about  $\lambda_{\text{ex}}=230\text{nm}$  and  $\lambda_{\text{ex}}=290\text{nm}$  corresponding to proteinaceous material.

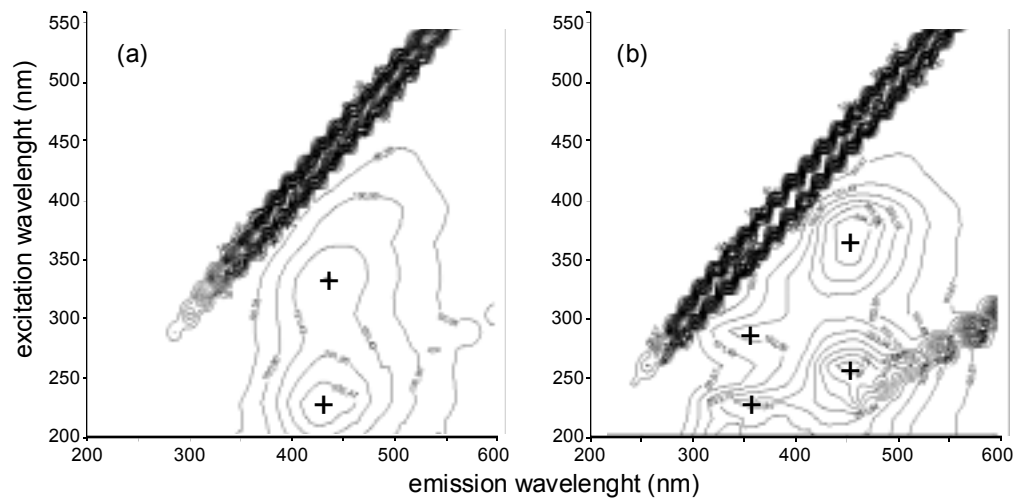


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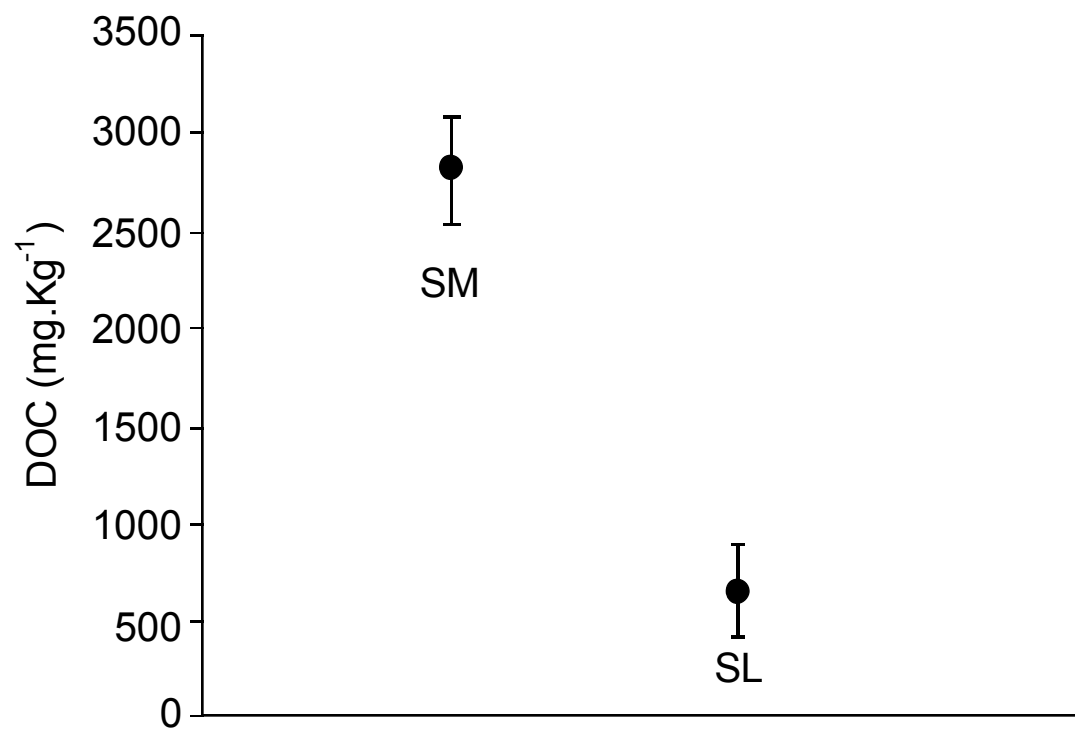


Fig. 8 : Organic Carbon contents from soil-water extracts in the Salina do Meio (SM) and Salitrada (SL) lakes.

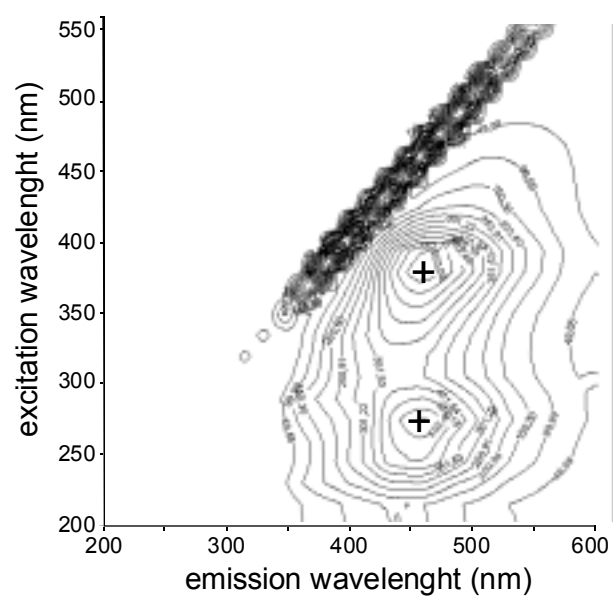


Fig. 9 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salina do Meio (SM) – Note the similarity with Fig. 6 and disappearance of peaks of proteinaceous material.



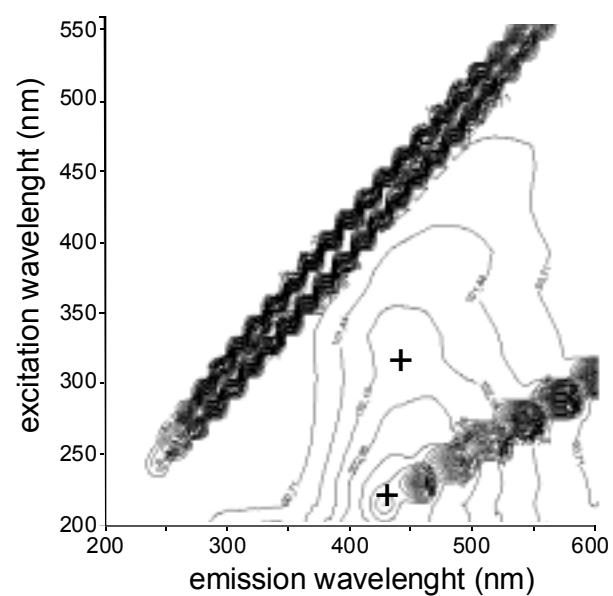


Fig. 10 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salitrada (SL) – Note the similarity with Fig. 4.

Table 1. Dissolved organic matter’s characteristics

Water body	Number of samples	$\lambda_{\text{ex}}$ (nm)	$\lambda_{\text{em}}$ (nm)	F (a.u.)	[DOC] (mg L <sup>-1</sup> )
Banhado (B)	4	220	425.5→431.5	705→915	}47.2→52.6
		335	425.5→431.5	374→622	
Salitrada (SL)	7	220	422→424.5	232→332	}44.8→117.7
		320	422→424.5	112→141	
Salinas (SM, SO, SP)	21	230	333→355	207→711	}144.7→381.6
		290	342→362	133→438	
		260	433→458	125.8→585	
		380	450→484	161.1→463	
	2	230	431→438	300	}105.7→143.3
		350	431→438	181.4→241.5	

$\lambda_{\text{ex}}$ : excitation wavelength;  $\lambda_{\text{em}}$ : emission wavelength; F (arbitrary units): fluorescence intensity